



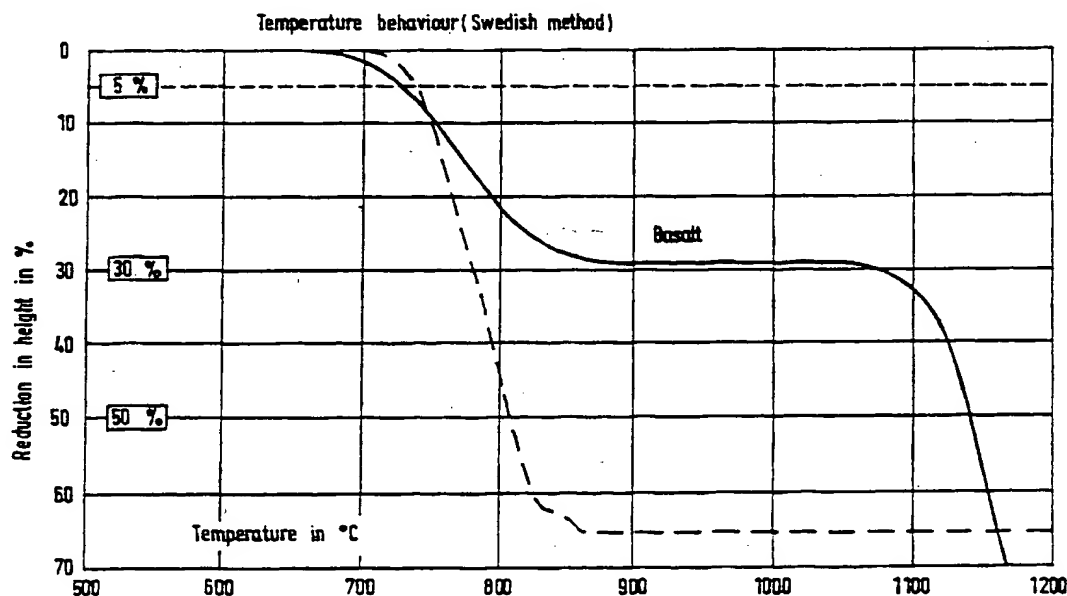
PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | | |
|--|--|---|--|
| (51) International Patent Classification ⁶ : C03C 13/00 | | A1 | (11) International Publication Number: WO 95/31410 |
| | | | (43) International Publication Date: 23 November 1995 (23.11.95) |
| (21) International Application Number: PCT/EP95/01842 | | (81) Designated States: AU, BR, CA, CN, CZ, FI, HU, JP, KR, NO, NZ, PL, SI, SK, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). | |
| (22) International Filing Date: 16 May 1995 (16.05.95) | | | |
| (30) Priority Data: P 44 17 230.3 17 May 1994 (17.05.94) DE 195 03 169.5 1 February 1995 (01.02.95) DE | | Published With international search report. | |
| (71) Applicant (for all designated States except US): ISOVER SAINT-GOBAIN [FR/FR]; Les Miroirs, 18, avenue d'Alsace, F-92400 Courbevoie (FR). | | | |
| (72) Inventors; and | | | |
| (75) Inventors/Applicants (for US only): LOHE, Peter [DE/DE]; Ritterstrasse 5, D-67112 Mutterstadt (DE). HOLSTEIN, Wolfgang [DE/DE]; Herderstrasse 2, D-35315 Homberg (DE). SCHWAB, Wolfgang [DE/DE]; Schönaauer Strasse 25, D-68723 Plankstadt (DE). MAUGENDRE, Stéphane [FR/FR]; 21, rue Gaston-Watteau, F-60460 Précly-sur-Oise (FR). | | | |
| (74) Agent: KADOR & PARTNER; Corneliusstrasse 15, D-80469 Munich (DE). | | | |

(54) Title: A MINERAL-FIBER COMPOSITION



(57) Abstract

A mineral-fiber composition that is biologically degradable characterized by the following constituents in percent by weight: SiO₂ 40 to 67, CaO 20 to 45, MgO 0 to 12, Na₂O 0 to 10, B₂O₃ 0 to 15, Na₂O + B₂O₃ 0 to 25, P₂O₅ 0 to 5, Al₂O₃ 0 to 3, TiO₂, Fe₂O₃, BaO, MnO, K₂O 0 to 5.

A mineral-fiber composition

The present invention relates to a mineral-fiber composition that is biologically degradable.

The prior art describes some mineral-fiber compositions which are said to be biologically degradable.

The biological degradability of mineral-fiber compositions is of great importance because various studies point out that mineral fibers with very small diameters in the range of less than 3 microns are suspected to be carcinogenic, while biologically degradable mineral fibers of such dimensions show no carcinogenicity.

However not only the biological degradability is of crucial importance but also the mechanical and thermal properties of the mineral fibers, or the products produced therefrom, and the processibility of the mineral-fiber composition. For example mineral fibers are used to a great extent for insulation purposes. In particular for application in the industrial area sufficient temperature stability of the mineral fibers is necessary.

Also, the mineral-fiber composition must permit processibility by known methods for producing mineral fibers with a small diameter, for example the jet process.

The invention is based on the problem of providing a novel mineral-fiber composition that is characterized by biological degradability, has good temperature stability and is easy to process.

The invention is based on the finding that this problem can be solved by a mineral-fiber composition that comprises substantially silicon oxide and alkaline earth oxides and that also contains boron oxide or barium oxide.

It has turned out that such mineral-fiber compositions fulfill the combination of the necessary properties, namely biological degradability, temperature stability and good processibility.

The object of the invention is a mineral-fiber composition that is biologically degradable, characterized by the following constituents in percent by weight:

| | | |
|--|----|-------|
| SiO ₂ | 40 | to 67 |
| CaO | 20 | to 45 |
| MgO | 0 | to 12 |
| Na ₂ O | 0 | to 10 |
| B ₂ O ₃ | 0 | to 15 |
| Na ₂ O + B ₂ O ₃ | 0 | to 25 |
| P ₂ O ₅ | 0 | to 5 |
| Al ₂ O ₃ | 0 | to 3 |
| TiO ₂ , Fe ₂ O ₃ , BaO, MnO, K ₂ O | 0 | to 5 |

The inventive mineral-fiber compositions are drawable by the jet process or the rotary process. The obtained fibers have good temperature stability. Surprisingly enough, the mineral-fiber compositions show biological degradability. The mean fiber diameter is preferably 10 microns or less, and especially between 2.5 and 5 microns.

The addition of boron oxide causes a lowering of the melting point and the formation of microcrystals resulting in better handling.

The inventive mineral-fiber compositions preferably have the following constituents in percent by weight:

| | | |
|--|-----|-------|
| SiO ₂ | 40 | to 67 |
| CaO | 20 | to 45 |
| MgO | 0 | to 12 |
| Na ₂ O | 0 | to 10 |
| B ₂ O ₃ | 0.5 | to 15 |
| Na ₂ O + B ₂ O ₃ | 1 | to 15 |
| P ₂ O ₅ | 0 | to 5 |
| Al ₂ O ₃ | 0 | to 3 |
| TiO ₂ , Fe ₂ O ₃ , BaO, MnO, K ₂ O | 0 | to 5 |

A content of silicon oxide in the range of 53 to 58 percent by weight is particularly preferred.

With respect to the boron oxide a range of 3 to 8 percent by weight is particularly preferred, in particular 4 to 6 percent is advantageous.

In a preferred embodiment the aluminum oxide content can be 1 to 3 percent by weight, preferably 2 to 3 percent by weight. In another preferred embodiment, however, it is less than 1 percent by weight.

A further preferred mineral-fiber composition has the following constituents in percent by weight:

| | | |
|--------------------------------|-----|-------|
| SiO ₂ | 50 | to 60 |
| CaO | 25 | to 35 |
| MgO | 1 | to 10 |
| Na ₂ O | 1 | to 8 |
| P ₂ O ₅ | 0 | to 3 |
| Al ₂ O ₃ | 0 | to 2 |
| BaO | 0.5 | to 5. |

To assess biological degradability the standard powder test of the German Glass Society was used. This is an easily conducted method and gives a sufficient measure of biological degradability. The method is described in L. Springer, "Laboratoriumsbuch für die Glasindustrie", 3rd edition, 1950, Halle/S: W. Knapp Verlag.

The temperature behavior of the mineral fibers was determined by the Swedish method. In this method a silit tube furnace is used with a horizontal working tube open on both sides having a length of 350 mm and an inside diameter of 27 mm. In the center of the furnace there is a small ceramic supporting plate (30 X 20 X 3 mm) for holding the test sample. The test sample has dimensions of 12 X 12 X 12 mm or 12 mm ϕ X 12 mm height. The bulk density is normally 100 kg/m³. The temperature

increase is 5 K/min. The change in test sample height is determined continuously with a reading optic.

The invention shall be described in more detail in the following with reference to examples.

Example 1

A mineral wool of the following composition in percent by weight was produced:

| | |
|--------------------------------|------|
| SiO ₂ | 50 |
| Al ₂ O ₃ | 0.8 |
| Fe ₂ O ₃ | 0.3 |
| CaO | 41.1 |
| MgO | 0.6 |
| Na ₂ O | 0.4 |
| K ₂ O | 0.1 |
| B ₂ O ₃ | 5.2 |

This composition could be processed well to mineral fibers with a mean diameter of 2.7 microns by the jet process at a drawing temperature of 1360°C.

An investigation according to the standard powder test of the German Glass Society yielded a value of 35 mg/kg and thus a value for high biological degradability.

Determination of temperature behavior by the Swedish method yielded a temperature stability at 5% reduction in height of 740°C, which can be clearly seen from the corresponding diagram shown by way of example in the single drawing.

Example 2

A mineral wool with the following composition in percent by weight was produced:

| | |
|--------------------------------|------|
| SiO ₂ | 56.5 |
| Al ₂ O ₃ | 0.3 |
| Fe ₂ O ₃ | 0.3 |
| CaO | 29.1 |
| MgO | 7.8 |
| Na ₂ O | 0.5 |
| B ₂ O ₃ | 5.0. |

This composition could be processed well to mineral fibers with a mean diameter of 2.8 microns by the jet process at a drawing temperature of 1320°C.

An investigation according to the standard powder test of the German Glass Society yielded a value of 39 mg/kg and thus a value for high biological degradability.

Determination of temperature behavior by the Swedish method yielded a temperature stability at 5% reduction in height of 720°C.

Example 3

A mineral wool with the following composition in percent by weight was produced:

| | |
|--------------------------------|------|
| SiO ₂ | 51.5 |
| Fe ₂ O ₃ | 0.3 |
| Al ₂ O ₃ | 2.0 |
| CaO | 28 |
| MgO | 10 |
| Na ₂ O | 6.4 |
| K ₂ O | 0.5 |

B₂O₃ 0.5.

This composition could also be processed well to mineral fibers with a mean diameter of 2.9 microns by the jet process at a drawing temperature of 1340°C.

An investigation according to the standard powder test of the German Glass Society yielded a value of 33 mg/kg and thus a value for high biological degradability.

Determination of temperature behavior by the Swedish method yielded a temperature stability at 5% reduction in height of 700°C.

Example 4

A mineral wool with the following composition in percent by weight was produced:

| | |
|--------------------------------|------|
| SiO ₂ | 51.2 |
| Fe ₂ O ₃ | 0.5 |
| Al ₂ O ₃ | 1.9 |
| CaO | 26.8 |
| MgO | 9.3 |
| Na ₂ O | 7.3 |
| K ₂ O | 0.5 |
| B ₂ O ₃ | 1.4. |

This composition could be processed well to mineral fibers with a mean diameter of 2.5 microns by the jet process at a drawing temperature of 1340°C.

An investigation according to the standard powder test of the German Glass Society yielded a value of 37 mg/kg and thus a value for high biological degradability.

Determination of temperature behavior by the Swedish method yielded a temperature stability at 5% reduction in height of 700°C.

Example 5

A mineral wool with the following composition in percent by weight was produced:

| | |
|--------------------------------------|------|
| SiO ₂ | 56 |
| Fe ₂ O ₃ | 0.3 |
| Al ₂ O ₃ | 0.3 |
| CaO | 27.4 |
| MgO | 7 |
| Na ₂ O | 4.5 |
| K ₂ O | 0.5 |
| Na ₂ O + K ₂ O | 5 |
| BaO | 4. |

This composition could be processed well to mineral fibers with a mean diameter of 2.7 microns by the jet process at a drawing temperature of 1360°C.

An investigation according to the standard powder test of the German Glass Society yielded a value of 35 mg/kg and thus a value for high biological degradability.

Determination of temperature behavior by the Swedish method yielded a temperature stability at 5% reduction in height of 740°C.

Example 6

A mineral wool with the following composition in percent by weight was produced:

| | |
|--------------------------------|------|
| SiO ₂ | 55.5 |
| Fe ₂ O ₃ | 0.4 |
| Al ₂ O ₃ | 0.5 |
| CaO | 27.1 |

| | |
|--------------------------------------|-----|
| MgO | 7.5 |
| Na ₂ O | 5.5 |
| K ₂ O | 0.5 |
| Na ₂ O + K ₂ O | 6 |
| BaO | 3. |

This composition could be processed well to mineral fibers with a mean diameter of 2.8 microns by the jet process at a drawing temperature of 1350°C.

An investigation according to the standard powder test of the German Glass Society yielded a value of 39 mg/kg and thus a value for high biological degradability.

Determination of temperature behavior by the Swedish method yielded a temperature stability at 5% reduction in height of 720°C.

Example 7

A mineral wool with the following composition in percent by weight was produced:

| | |
|--------------------------------|------|
| SiO ₂ | 56 |
| Al ₂ O ₃ | 1 |
| CaO | 28.5 |
| MgO | 7 |
| Na ₂ O | 5 |
| BaO | 2.5. |

This composition could be processed well to mineral fibers with a mean diameter of 2.7 microns by the jet process at a drawing temperature of 1350°C.

An investigation according to the standard powder test of the German Glass Society yielded a value of 35 mg/kg and thus a value for high biological degradability.

Determination of temperature behavior by the Swedish method yielded a temperature stability at 5% reduction in height of 720°C.

Example 8

A mineral wool with the following composition in percent by weight was produced:

| | |
|--------------------------------|----|
| SiO ₂ | 56 |
| Al ₂ O ₃ | 1 |
| CaO | 29 |
| MgO | 8 |
| Na ₂ O | 5 |
| BaO | 1. |

This composition could be processed well to mineral fibers with a mean diameter of 2.8 microns by the jet process at a drawing temperature of 1360°C.

An investigation according to the standard powder test of the German Glass Society yielded a value of 39 mg/kg and thus a value for high biological degradability.

Determination of temperature behavior by the Swedish method yielded a temperature stability at 5% reduction in height of 740°C.

Claims

1. A mineral-fiber composition that is biologically degradable, characterized by the following constituents in percent by weight:

| | | |
|--|----|-------|
| SiO ₂ | 40 | to 67 |
| CaO | 20 | to 45 |
| MgO | 0 | to 12 |
| Na ₂ O | 0 | to 10 |
| B ₂ O ₃ | 0 | to 15 |
| Na ₂ O + B ₂ O ₃ | 0 | to 25 |
| P ₂ O ₅ | 0 | to 5 |
| Al ₂ O ₃ | 0 | to 3 |
| TiO ₂ , Fe ₂ O ₃ , BaO, MnO, K ₂ O | 0 | to 5. |

2. The mineral-fiber composition of claim 1, characterized by the following constituents in percent by weight:

| | | |
|--|-----|-------|
| SiO ₂ | 40 | to 67 |
| CaO | 20 | to 45 |
| MgO | 0 | to 12 |
| Na ₂ O | 0 | to 10 |
| B ₂ O ₃ | 0.5 | to 15 |
| Na ₂ O + B ₂ O ₃ | 1 | to 15 |
| P ₂ O ₅ | 0 | to 5 |
| Al ₂ O ₃ | 0 | to 3 |
| TiO ₂ , Fe ₂ O ₃ , BaO, MnO, K ₂ O | 0 | to 5. |

3. The mineral-fiber composition of claim 1, characterized by the following constituents in percent by weight:

| | | |
|--|--------------|-------|
| SiO ₂ | 45 | to 60 |
| CaO | 25 | to 45 |
| MgO | 5 | to 10 |
| Na ₂ O | 0 | to 5 |
| B ₂ O ₃ | 1 | to 15 |
| Na ₂ O + B ₂ O ₃ | 3 | to 10 |
| P ₂ O ₅ | 0 | to 1 |
| Al ₂ O ₃ | 0 | to 3 |
| TiO ₂ , Fe ₂ O ₃ , BaO, MnO, K ₂ O | 0 | to 3 |
| Fe ₂ O ₃ | less than 1. | |

4. The mineral-fiber composition of any of claims 1 to 3, characterized in that the amount of silicon oxide is 53 to 58 percent by weight.

5. The mineral-fiber composition of any of claims 1 to 3, characterized in that the amount of boron oxide is 3 to 8 percent by weight, in particular 4 to 6 percent by weight.

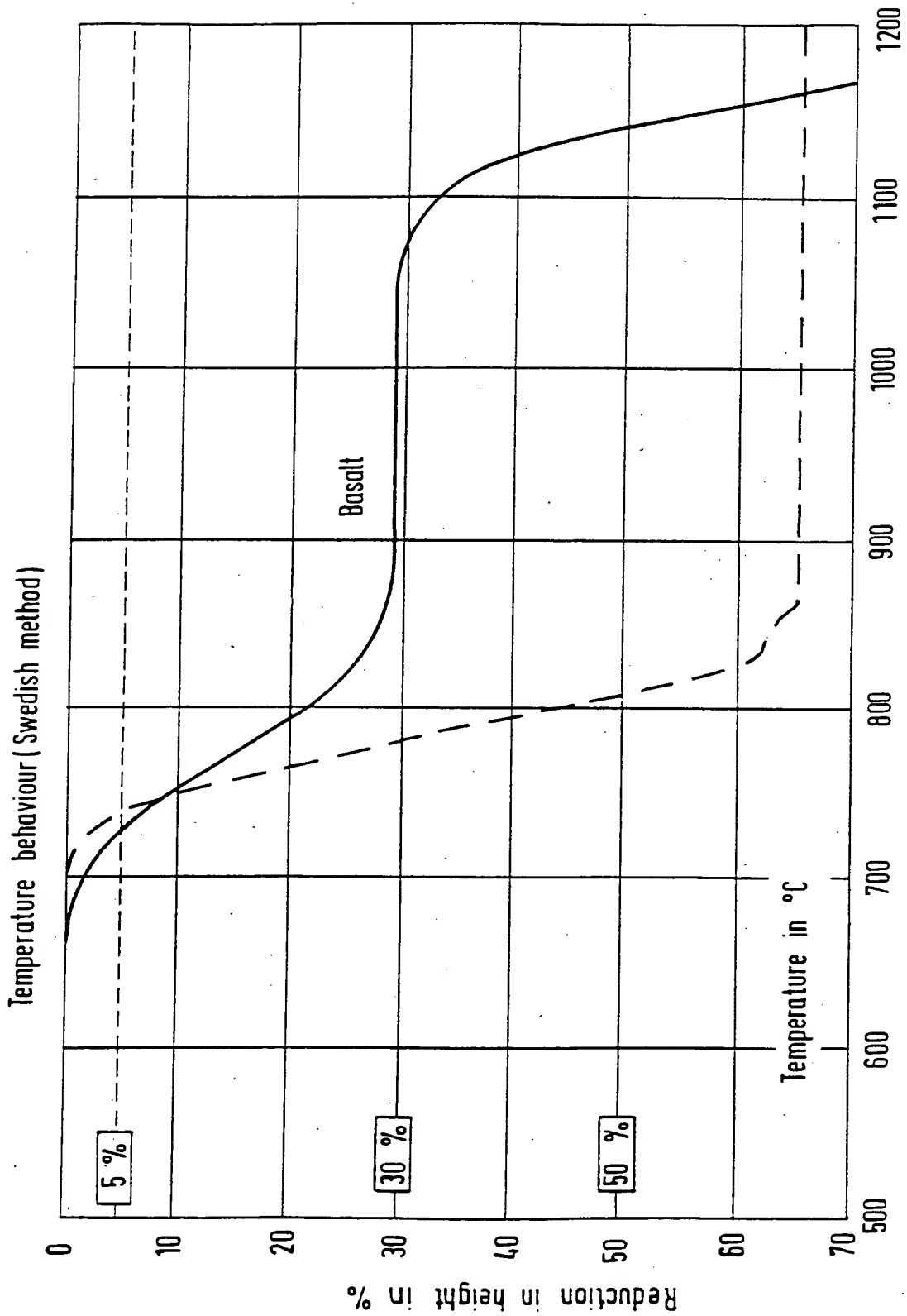
6. The mineral-fiber composition of claim 1, characterized by the following constituents in percent by weight:

| | | |
|--------------------------------|-----|-------|
| SiO ₂ | 50 | to 60 |
| CaO | 25 | to 35 |
| MgO | 1 | to 10 |
| Na ₂ O | 1 | to 8 |
| P ₂ O ₅ | 0 | to 3 |
| Al ₂ O ₃ | 0 | to 2 |
| BaO | 0.5 | to 5. |

7. The mineral-fiber composition of claim 6, characterized by the following constituents in percent by weight:

| | | |
|--------------------------------|-----|--------|
| SiO ₂ | 52 | to 58 |
| CaO | 28 | to 32 |
| MgO | 5 | to 10 |
| Na ₂ O | 3 | to 7 |
| P ₂ O ₅ | 0 | to 1 |
| Al ₂ O ₃ | 0.5 | to 1.5 |
| BaO | 0.5 | to 3. |

1/1



INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/EP 95/01842

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| X | WO,A,89 12032 (MANVILLE SALES CORPORATION) 14 December 1989 test nos. 164-171, 194, 197-199, 201, 203, 204, 206, 207, 209, 217-225 see table 3 | 1-3,5 |
| A | --- | 4,6,7 |
| X | GB,A,2 083 017 (NIPPON SHEET GLASS CO., LTD.) 17 March 1982 see page 2, line 11 - line 64; examples 14-16,18,19 | 1-3,5 |
| A | --- | 4,6,7 |
| X | FR,A,2 690 438 (ISOVER SAINT-GOBAIN) 29 October 1993 see claim 1; examples 6,9 | 1,4 |
| A | --- | 2,3,5-7 |
| | --- -/-- | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

- * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- * "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- * "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- * "&" document member of the same patent family

Date of the actual completion of the international search

9 August 1995

Date of mailing of the international search report

31.08.95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Van Bommel, L

INTERNATIONAL SEARCH REPORT

Intern. Application No.
PCT/EP 95/01842

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|-----------------------|
| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X | WO,A,92 09536 (PAROC OY AB) 11 June 1992 see examples IA, IB, C | 1,4 |
| A | --- | 2,3,5-7 |
| X | WO,A,93 15028 (THE MORGAN CRUCIBLE COMPANY PLC) 5 August 1993 see table 3 | 1,4 |
| A | --- | 2,3,5-7 |
| X | WO,A,87 05007 (MANVILLE CORPORATION) 27 August 1987 see claim 10; Table I, fibers D, F, H, J; Table II: fibers A-C, F-I | 1,4 |
| A | ----- | 2,3,5-7 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No.

PCT/EP 95/01842

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| WO-A-8912032 | 14-12-89 | AU-A- 3765789 | 05-01-90 |
| | | US-A- 5332699 | 26-07-94 |
| GB-A-2083017 | 17-03-82 | JP-C- 1473801 | 27-12-88 |
| | | JP-A- 57047741 | 18-03-82 |
| | | JP-B- 63020780 | 30-04-88 |
| | | US-A- 4443550 | 17-04-84 |
| FR-A-2690438 | 29-10-93 | AU-B- 4263293 | 29-11-93 |
| | | BR-A- 9305492 | 11-10-94 |
| | | CA-A- 2110998 | 11-11-93 |
| | | CN-A- 1078708 | 24-11-93 |
| | | CZ-A- 9302865 | 19-10-94 |
| | | EP-A- 0596088 | 11-05-94 |
| | | WO-A- 9322251 | 11-11-93 |
| | | HU-A- 67212 | 28-03-95 |
| | | JP-T- 6508600 | 29-09-94 |
| | | NO-A- 934725 | 20-12-93 |
| | | SI-A- 9300218 | 31-12-93 |
| WO-A-9209536 | 11-06-92 | FI-B- 93346 | 15-12-94 |
| | | AT-T- 117662 | 15-02-95 |
| | | AU-A- 8908791 | 25-06-92 |
| | | DE-D- 69107091 | 09-03-95 |
| | | EP-A- 0558548 | 08-09-93 |
| WO-A-9315028 | 05-08-93 | AU-B- 3358493 | 01-09-93 |
| | | CA-A- 2127357 | 05-08-93 |
| | | EP-A- 0621858 | 02-11-94 |
| | | FI-A- 943380 | 14-09-94 |
| | | GB-A- 2277516 | 02-11-94 |
| | | HU-A- 68033 | 29-05-95 |
| | | JP-T- 7502969 | 30-03-95 |
| | | NO-A- 942655 | 14-07-94 |
| | | ZA-A- 9300311 | 23-08-93 |
| WO-A-8705007 | 27-08-87 | AU-B- 590393 | 02-11-89 |
| | | AU-A- 6948887 | 09-09-87 |
| | | CA-A- 1271785 | 17-07-90 |
| | | EP-A- 0257092 | 02-03-88 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/EP 95/01842

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| WO-A-8705007 | | FI-B- 94520 | 15-06-95 |
| | | JP-B- 7042139 | 10-05-95 |
| | | JP-T- 63502746 | 13-10-88 |
| | | US-A- 5332699 | 26-07-94 |
| ----- | | | |